Supporting Information

Measurements of Isoprene-Derived Organosulfates in Ambient Aerosols by Aerosol Time-of-Flight Mass Spectrometry, Part 2: Temporal Variability and Formation Mechanisms

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This supporting information contains 9 pages and 4 figures.

Experimental

ATOFMS Measurements and Analysis.

For both the ANARChE and AMIGAS datasets considered here, some negative spectra displayed incorrect mass calibration in the mass range of interest (>100 *m/z*) due to instability in the mass spectrometer voltages. As a result, the majority (~ 90-95%) of particles containing organosulfates during AMIGAS (~50% during ANARChE) displayed a slight shift in *m/z* relative to the true value. Because the shift in *m/z* becomes more exaggerated at higher *m/z* due to the longer flight time in the TOF mass analyzer, the high-mass organosulfate peaks were impacted to a greater degree. In order to ensure data quality, a detailed analysis method was adopted for AMIGAS as follows. ART-2a clusters containing the proposed organosulfate markers were identified and each cluster was divided up by day. An average spectrum was obtained for each cluster on each day and the actual *m/z* (m/z_{actual}) of the peaks in question were identified by using known markers as an indication of the mass calibration. To determine mass spectral peak area as a function of time and/or particle size, the peak area search was performed on m/z_{actual} for each cluster on each day and the results from different clusters were combined accordingly. The ANARChE data was treated similarly, except the ART-2a clusters were treated intact and were not divided by day since the calibration issues were less severe than during AMIGAS.

Results and Discussion

Temporal trends of organosulfate markers. The temporal profiles during AMIGAS of the organosulfate markers at *m/z* -215, -199, -155, and -153 are included in Figure S1. For the latter three ions, the diurnal trends are somewhat less definitive than *m/z* -215, however in general

these markers track reasonably well, typically peaking overnight. Correlation plots between the markers can be found in Hatch et al.[1]

Nocturnal acid-catalyzed organosulfate formation. The overnight formation of organosulfates observed in Atlanta is proposed to occur by acid-catalyzed reactive uptake, as the only other currently known formation mechanism requires radiation to form sulfate/bisulfate radicals[2]. While several observations seem to support this hypothesis, data from ANARChE and AMIGAS are not in full agreement. During AMIGAS, both the particle size and temporal trends demonstrate a relationship of increasing IEPOX-derived organosulfate with increasing *m/z* -195. The size distribution shows that the organosulfate and sulfuric acid concentrations increased as particle size decreased (R^2=0.83, Figure S1), consistent with previous ATOFMS results that showed that particle phase acidity was highest at the smallest particle sizes[3]. Further, the correlation between these species in hourly time resolution is shown in Figure S2 for both daytime (6am – 6pm) and nighttime (6pm-6am) trends. A higher correlation was observed for the nighttime absolute peak area trend (R^2=0.56) than the daytime trend (R^2=0.36), possibly indicating a stronger relationship between acidity and organosulfate formation overnight. Further, the segregation of the day and night trends in the correlation plot, with a higher slope occurring overnight (1.13 vs. 0.66), suggests that organosulfate production may be driven largely by IEPOX uptake, as the increase in IEPOX gas-to-particle partitioning at night led to increased organosulfate formation for a given acidity level than would occur during the daytime under a reduced uptake regime.

In contrast to AMIGAS, the temporal trends in the absolute areas of *m/z* -215 and -195 during ANARChE are anti-correlated (Figure S3), with *m/z* -195 peaking in the afternoon before the overnight increase in *m/z* -215. However, in this case, there are often increases in SO_2

concurrent with the increase in *m/z* -215, which perhaps contributed to the higher levels of organosulfates observed during periods of low *m/z* -195 peak area.

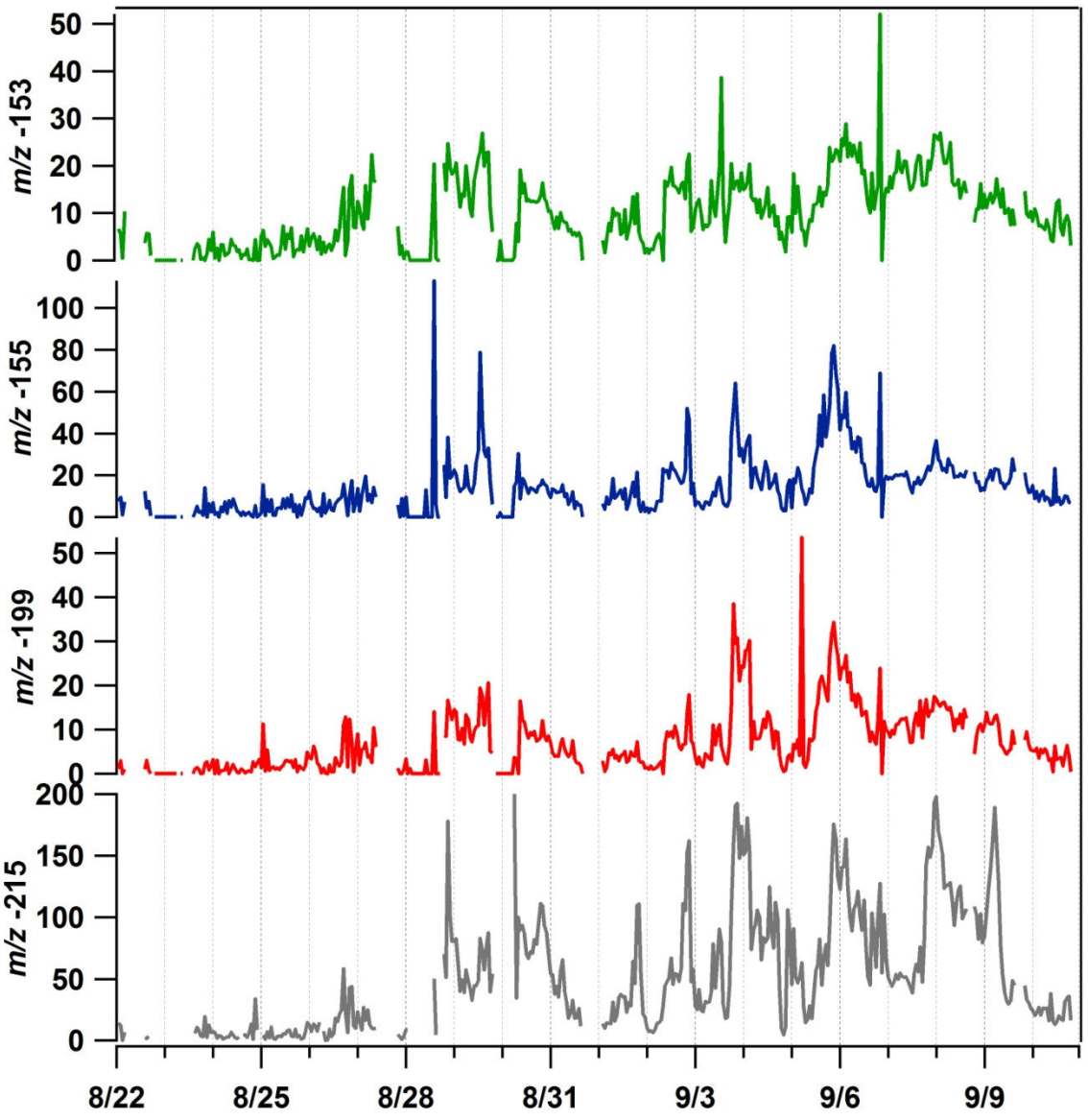

Figure S1. Hourly-averaged temporal variability in the absolute peak area of *m/z* -215 (gray), -199 (red), -155 (blue) and -153 (green) during AMIGAS.

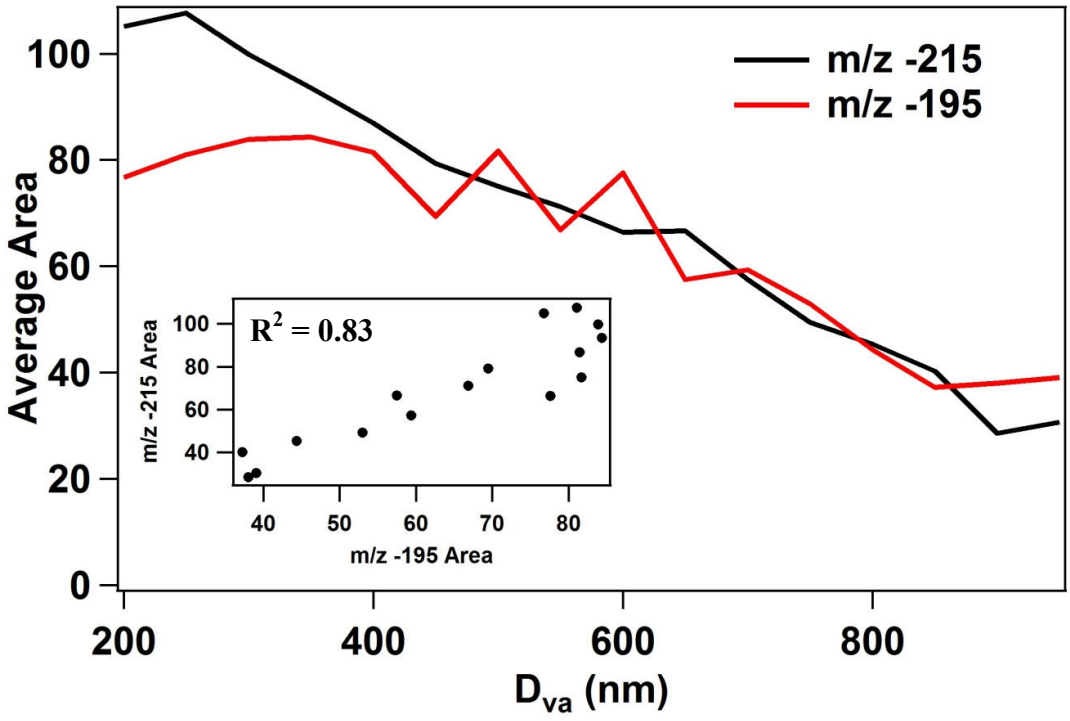

Figure S2. Size-dependence of *m/z* -215 and -195 absolute peak areas averaged over 50 nm size bins for the AMIGAS dataset. The inset shows the correlation between the two species as a function of size (R^2=0.83).

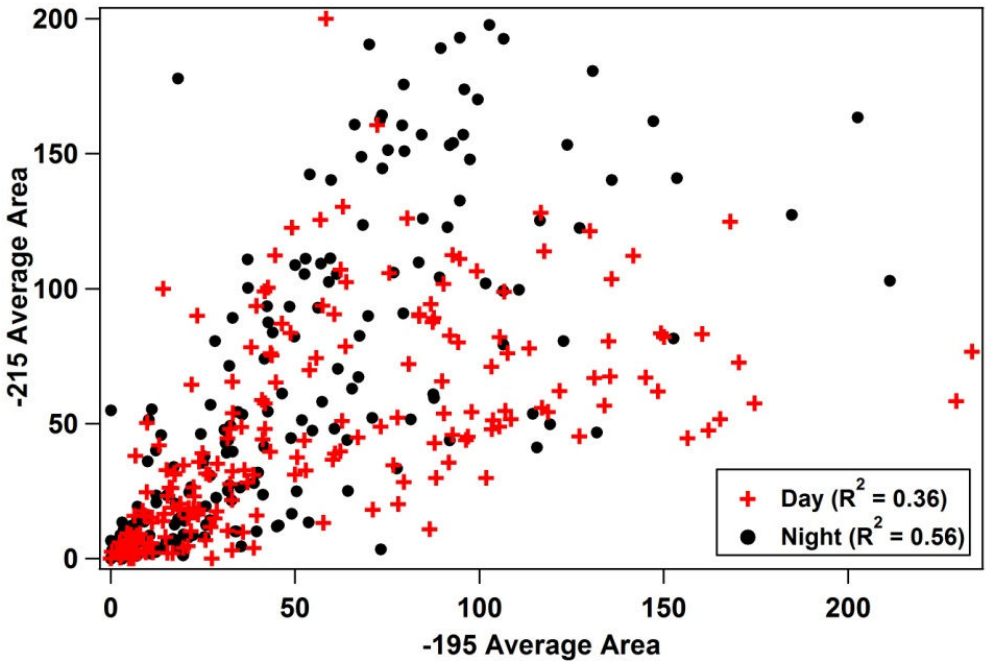

Figure S3. Daytime (6am-6pm; red) and nighttime (6pm-6am; black) correlation plots of the hourly-averaged absolute peak areas of *m/z* -215 (IEPOX-OS) and *m/z* -195 ($H_2SO_4HSO_4^-$) during AMIGAS.

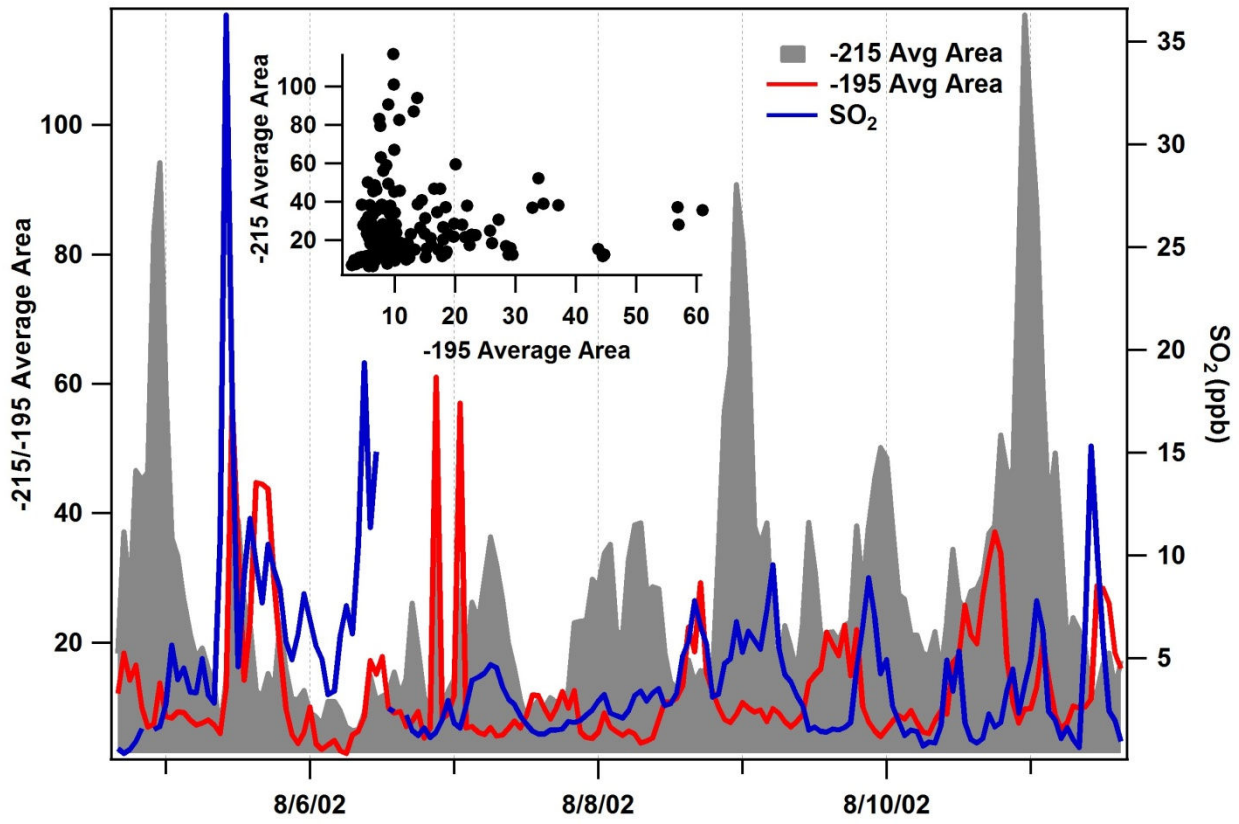

Figure S4. Temporal trends during ANARChE of the hourly-averged absolute area of *m/z* -215, m/z -195, and SO_2. The inset shows the correlation between *m/z* -215 and -195.

References

1. Hatch, L. E.; Creamean, J. M.; Ault, A. P.; Surratt, J. D.; Chan, M. N.; Seinfeld, J. H.; Edgerton, E. S.; Su, Y.; Prather, K. A., Measurements of Isoprene-Derived Organosulfates in Ambient Aerosols by Aerosol Time-of-Flight Mass Spectometry - Part 1: Single Particle Atmospheric Observations in Atlanta. *Environ. Sci. Technol.* **2011,** *45*, (12), 5105 - 5111.

2. Noziére, B.; Ekström, S.; Alsberg, T.; Holmström, S., Radical-initiated formation of organosulfates and surfactants in atmospheric aerosols. *Geophys. Res. Lett.* **2010,** *37*.

3. Denkenberger, K. A.; Moffet, R. C.; Holecek, J. C.; Rebotier, T. P.; Prather, K. A., Real-time, single-particle measurements of oligomers in aged ambient aerosol particles. *Environ. Sci. Technol.* **2007,** *41*, (15), 5439-5446.